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Smectic bimetallomesogens: synthesis, characterization and mesomorphic properties and the crystal structure of bis[*N*-(3-hydroxypropyl)-4-octanoylsalicylaldiminato]copper(II) complex

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The synthesis, characterization and mesomorphic properties of copper(II), palladium(II), vanadyl(IV) and iron(III) chloride complexes derived from salicylaldimine structures are reported. The copper and palladium complexes exhibited smectic A phases, however vanadyl and iron chloride complexes showed crystalline phase. The palladium complexes have lower melting and clearing points, and a wider temperature range of mesophase. This lowering in clearing points between $M = \mathrm{Pd}$ and $M = \mathrm{Cu}$ analogues was attributed to the weaker core–core interaction between palladium centres within layers in the mesophase. The crystal and molecular structures of bis[*N*-(3-hydroxypropyl)-4-octanoylsalicylaldiminato]copper(II) were determined by means of X-ray analysis. This complex crystallizes in the monoclinic space group $p2_1/c$, with $a = 5.4908(23)$ Å, $b = 19.847(5)$ Å, $c = 16.636(4)$ Å, $\beta = 96.87(3)°$, and $Z = 2$. The intramolecular separation of Cu–Cu atoms is 3.022(3) Å. The structure shows that the molecular shape is nearly flat with two copper atoms lying 0.067(4) Å above and below the plane of N1, O1a, O1 and O2 atoms.

1. Introduction

While extensive research on the correlation between molecular structures and bulk material properties continues, the exploitation of new material will enhance successful technological applications. In metal-containing liquid crystals [1] (MLCs), the induction of liquid crystallinity by incorporation of a single metal centre or of multi-metal centres has attracted much research attention [2]. A variety of geometric shapes in metal centres may generate new mesophases with novel superstructures. These so called metallomesogens [3] are especially important since materials of this type promise to expand the range of technological applications and physical properties exhibited by traditional liquid crystals due to the rich electronic states inherent in the metal centres.

Our interest is in generating metallomesogenic materials containing multiple metal centres [4]. The focus is not only on the liquid crystalline behaviour but also on many potential properties produced by these expanded mesogenic cores. The question—whether the formation of novel mesophases is induced by various molecular structures created by incorporating multinuclear centres, or/and whether the possible physical properties [5] originate from the interaction between metal centres—remains to be investigated and answered. The appropriate molecular design and successful synthesis of polymetallomesogenic materials becomes a significant step towards an answer.

Recently, we have been investigating the liquid crystalline behaviour in expanded bimetallomesogenic core structures [4], for example, complexes with two metal centres existing either in close promimity (e.g. complex **1** and **2** [4(*d*)]) or more remote (e.g. complex **3** [4(*a*)]). We hope better to understand the role of multiple metal centres in the formation of liquid crystals as well as their resulting physical properties.

Most bimetallomesogens reported in the literature [3, 4] consist of disc-like molecules and only a few of rod-like molecules; these bimetallic complexes exhibit columnar discotic phases [3(*c*, *d*)] and smectic phases [3(*h*, *j*)], respectively. In this report we describe the synthesis and mesomorphic properties of a group of compounds comprising the copper, palladium, vanadyl and iron chloride complexes of two homologous series of *N*-(3-hydroxypropyl)-4-alkoxysalicylaldimines and *N*-(3-hydroxypropyl)-4-(4-alkoxybenzoyl)salicylaldimines, (**4**, **5** and **6**) as shown below.

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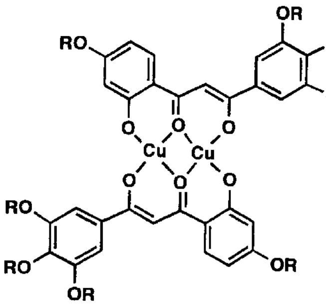
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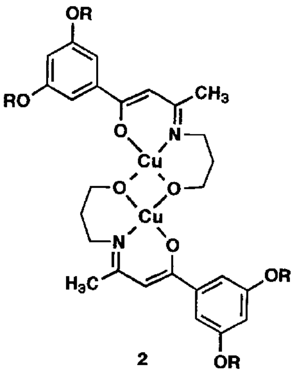
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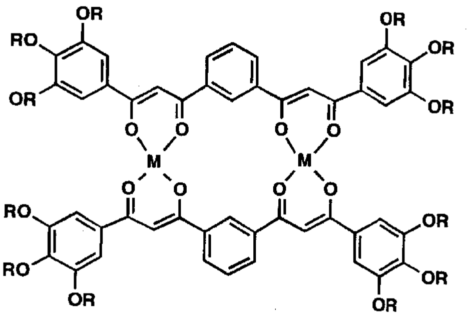
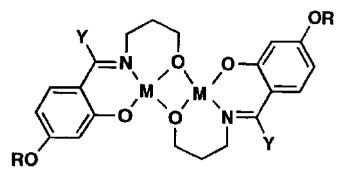
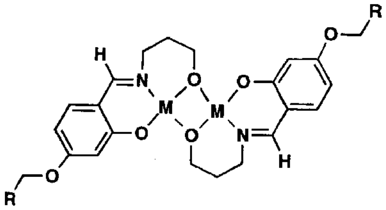

3 M = Cu, VO


R = $(CH_2)_nH$

4; Y= H; M = Cu, VO, Pd, FeCl

5; Y= CH_3; M = Cu, VO; n = 18


6; M = Cu, Pd; R = (*p*-alkoxyphenyl)

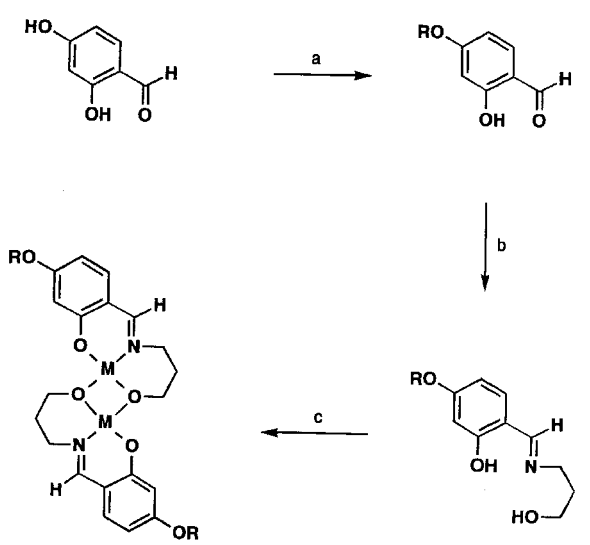
2. Results and discussion

2.1. *Synthesis and characterization*

The synthetic procedures for the metal complexes are shown in schemes 1 and 2. Literature procedures [6] for monoalkylation of 2,4-dihydroxybenzaldehyde were slightly modified to improve product yields. 4-Alkoxy-2-hydroxybenzaldehydes all consist of white needle crystals, however 4-(4-alkoxybenzoyl)-2-hydroxybenzaldehydes are colourless liquids for $n = 6, 8, 10$, and are white solids for $n = 12, 14, 16, 18$. Upon long exposure to moist air these compounds changed slowly in colour to purple due to partial conversion to diols. *N*-(3-Hydroxypropyl)-4-alkoxy-2-hydroxysalicylaldimines and *N*-(3-hydroxypropyl)-4-(4-alkoxybenzoyl)-2-hydroxysalicylaldimines were prepared in yields of 92–95% by condensation of appropriate 2-hydroxybenzaldehydes with 3-amino-1-propanol under reflux in chloroform/methanol, with added catalytic glacial acetic acid. Light yellow needle crystals of these Schiff's bases were identified by ^1H and ^{13}C NMR spectroscopy.

The disappearance of a sharp peak at *c.* 9.68 ppm characteristic of benzaldehyde hydrogen (H–C=O), and appearance of another sharp peak at *c.* 8.10 ppm characteristic of imine hydrogen (H–C=N), confirmed the formation of Schiff's bases.

Copper [7], vanadyl, palladium and iron chloride [8] complexes were obtained by reactions [7–9] of the Schiff's base with copper acetate, vanadyl sulphate pentahydrate, palladium acetate and anhydrous ferric chloride in chloroform/methanol or THF solution. The copper and vanadyl complexes are greyish to purple needle crystals; the palladium and iron chloride complexes are yellowish and red solids, respectively. The C=N stretching vibration of the Schiff's bases is located



Scheme 1. Reagents and Conditions: (a) RBr(1.1 eq) KI(cat.) refluxing in CH_3COCH_3, 24 h. 87-93%. (b) $H_2N(CH_2)_3OH$ (1.1 eq), CH_3COOH (5 drops), refluxing in CH_3Cl/CH_3OH, 3 h. 85-94%. (c) $M(OAc)_2$ ($M = Cu$, Pd), $VOSO_4$, or $FeCl_3$, refluxing in $CHCl_3/CH_3OH$ or THF, reflux, 2 h. 70-85%.

in the region of 1640–1625 cm^{-1}, and is shifted to a lower wavenumber, c. 1620 cm^{-1} for the copper complexes, c. 1608 cm^{-1} for the palladium complexes and 1609 cm^{-1} for the vanadyl complexes. The vanadyl complexes also exhibit a stretching band at c. 988 cm^{-1} of V=O bonding, indicating a monomeric [10] structure. The copper and vanadyl compounds are paramagnetic, with the ^1H and ^{13}C NMR spectra displaying only broad alkyloxy signals. Elemental analysis confirmed the bimetallic composition of the complexes.

2.2. *Mesomorphic properties of the copper complexes*

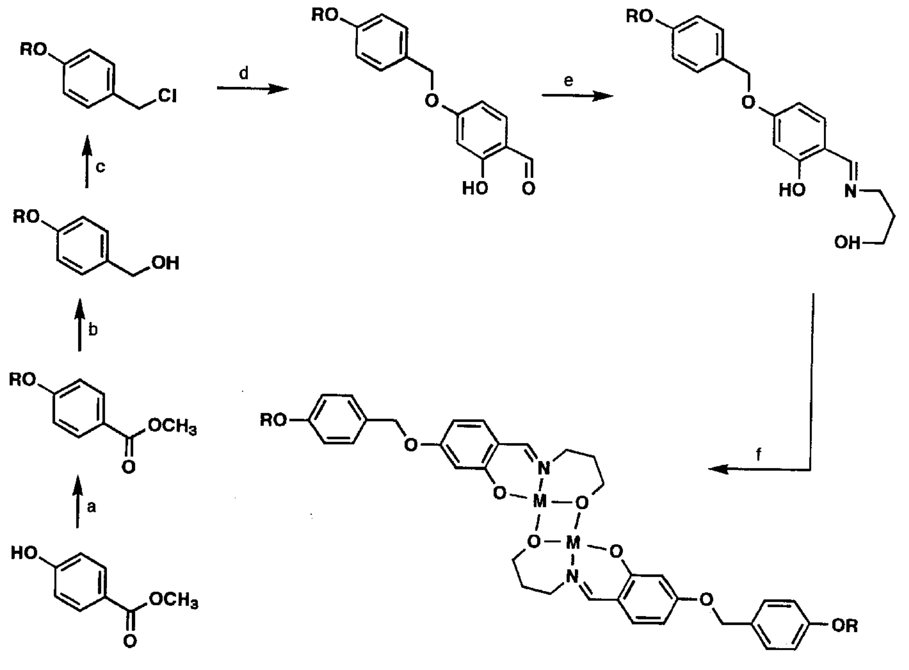
The liquid crystalline behaviour of all the bimetallic complexes was studied by thermal analysis (DSC) and polarizing microscopy. The phase transitions of metal complexes **4** and **5** are summarized in table 1. Copper complexes **4** exhibited monotropic behaviour. These complexes melt into isotropic liquid at temperatures of 150–191°C depending on the carbon chain length. However, the transition of isotropic to mesophase was observed only on cooling to within a temperature range of 124–145°C. The magnitude of transition enthalpies ranged from 0.24 to 1.73 kcal mol^{-1}, which was relatively small compared with the crystal to mesophase transition. The mesophase was identified as smectic A (SmA), based on optical texture [11]. A fan-shaped texture, figure 1 (*a*), on slowly cooling from the isotropic liquid was observed, typical for rod-like molecules. Also this smectic A phase was easily confirmed by the partial appearance of homeotropic texture, without subjecting the sample to mechanical stress. In this phase, the molecules may spontaneously align normal to the surface, giving a dark, essentially textureless field between crossed polarizers. Similar phase transitions were also observed for mononuclear [2(*b*)] complexes of Cu, Ni, Pd, Pt, VO and Fe with Schiff's bases derived from 4- or 5-substituted alkoxylsalicylaldehyde. These similar Schiff's base derivatives of rod-like compounds exhibited several smectic and/or nematic phases. With the bimetallic oxygen-bridged centre as the extended core in this system, longer and/or more carbon chains are expected for the formation of stable mesophases.

The formation and stability of the mesophase are also very sensitive to steric hindrance. For example, liquid crystallinity is totally suppressed in copper complexes **5**; presumably the increased bulk of a methyl group destroys the weak intermolecular force necessary to stabilize the liquid crystallinity of normal square planar coordination geometry of the copper(II) in favour of tetrahedral geometry. A crystal to isotropic transition at 188.1°C was observed for the copper complex **5** ($n = 18$).

Following the above observation, the copper complexes **6** which have longer tails were also prepared, and their mesomorphic properties studied to evaluate the effect of elongated benzoyl side chains at the 4-position on the formation and stability of mesophases. The phase behaviour for the copper and palladium complexes are summarized in table 2. The data indicate that the copper complexes **6**, $n = 12$ and 14, all exhibit enantiotropic behaviour; however complexes with $n = 8$, 10 and 18 show monotropic behaviour. The melting and clearing points for this series of complexes were comparatively higher than copper analogues **4**. The phases were identified as smectic A phases, based on observed textures; longer tails connected to the core group apparently stabilized the mesophases.

2.3. *Palladium complexes*

The transition temperatures and thermodynamic data for the palladium complexes **4** are given in table 1. All are thermally stable above the clearing temperature without decomposition; with $n > 8$, the complexes showed a liquid crystalline phase. Optical textures indicated that these palladium complexes exhibited enantiotropic smectic A phase behaviour. The palladium complexes were found to have much lower melting temperatures and slightly lower clearing points than the copper analogues. The temperature range of the mesophase was also slightly wider (40.0–73.0°C, on cooling) than those of copper analogues (5.0–17.0°C). The decrease in clearing points is attributed to the weaker core–core interaction. This difference in the melting and clearing points is shown in table 2, and was also observed in complexes **6**, $M = Cu$ and $M = Pd$, which all have



Scheme 2. Reagents and Conditions: (a) RBr(1.0 eq), K_2CO_3 (3.0 eq), refluxed in CH_3COCH_3, 24 h, 85-92%. (b) $LiAlH_4$(1.1 eq), stirred at RT in dried THF, 1 h, then refluxed 1/2 h, 83-95%. (c) $SOCl_2$ (1.1 eq), stirred in THF at RT, 10 min, 80-88%. (d) 2,4-dihydroxybenzaldehyde (1.0 eq), $KHCO_3$(1.1 eq), stirred at 50°C in CH_3COCH_3 24 h, 76-80%. (e) $H_2N(CH_2)_3OH$ (1.2 eq), refluxed in absolute C_2H_5OH, 3 h, 90-93%. (f) $M(OAc)_2$; M = Cu, Pd, refluxed in $CHCl_3$/CH_3OH, 2 h, 72-85%.

longer benzyloxy tails. The optical fan-shaped texture, (figure 1 (*b*)), similar to that of copper complexes **4**, was observed and identified as smectic A phase under the polarizing microscope. The preferred formation of smectic A over nematic phases in this system of bimetallic oxygen-bridged structures may result from the weak coordination force between the oxygen (or nitrogen) atom and metal centres within neighbouring molecules.

2.4. *Vanadyl and iron chloride complexes*

The incorporation of vanadyl and iron chloride centres into the core group might result in the generation of metal complexes with directional polar order. This type of polar order is particularly important for the formation of ferroelectric and NLO materials [1 (*d*)]. These complexes were considerably stable without any decomposition above isotropic temperatures.

Unfortunately, the vanadyl and iron chloride complexes prepared exhibited only crystal-to-isotropic transition. The IR stretching frequency of ν (V=O) at *c*. 988 cm^{-1} in vanadyl complexes at room temperature indicated a monomeric structure. The stronger interaction between square pyramidal V=O or Fe–Cl centres seemed to inhibit the formation of liquid crystallinity. Attempts to induce liquid crystallinity by either increasing the side chain carbon lengths or changing the substitution position of terminal side chains were unsuccessful. The relative geometric structure of the two vanadyl or iron chloride centres, *trans* or *cis*, which determines the direction of the local dipole of molecules in these oxygen-bridged complexes, was uncertain from our IR data. Similar imine complexes with binuclear Fe–Cl centres [7 (*a*)] adopted a *trans* structure, from X-ray data. Unfortunately, the attempted growth of single crystals for structural determination of this type of bivanadyl and iron chloride complex was unsuccessful.

2.5. *Crystal and molecular structures*

Single crystal X-ray structure analysis was performed at room temperature for copper complex (**1**; $n = 8$). The needle crystals were grown at a CH_2Cl_2/CH_3OH (2/5) interface, and this complex showed a smectic A phase between 132 and 137°C on cooling. Figure 2 shows the molecular structure with the atomic numbering scheme. Table 3 gives crystallographic data and structure refinement; table 4 gives bond distances and bond angles. The overall molecular shape is lathlike and nearly flat, with two copper atoms lying 3.022(3) Å apart; one copper atom lies 0.067(4) Å above and the other 0.067(4) Å below the molecular plane defined by atoms N1, O2, O1a and O1. The parallel distance between two molecular planes is 5.491(2) Å, which is far greater than the distance for any strong bonding interaction. Two different views of the crystal packing showing the layered smectic-like structures are presented in figure 3, revealing that the molecules are packed in a highly interdigitated layered structure.

3. Summary

We have prepared dicopper, dipalladium and divanadyl complexes of Schiff's bases derived from salicylaldimines with expanded bimetallic core structures. These complexes displayed smectic phases as expected for rod-like molecules. Experimental results indicated that the

Table 1. Phase behaviour[a] of metal complexes **4** and **5**.

Metal	*n*	Heating (top) Cooling (bottom)				
4 *M* = Cu	8	Cr	191.3 (6.16)			I
		Cr	132.3 (6.63)	SmA	137.2 (0.24)	I
	10	Cr	180.8 (11.3)			I
		Cr	129.4 (7.56)	SmA	145.2 (1.18)	I
	12	Cr	171.2 (11.0)			I
		Cr	127.1 (7.90)	SmA	144.4 (1.23)	I
	14	Cr	164.7 (13.0)			I
		Cr	117.9 (8.89)	SmA	140.4 (1.43)	I
	16	Cr	149.7 (7.67)			I
		Cr	121.3 (9.66)	SmA	133.9 (1.71)	I
	18	Cr	150.3 (1.62)			I
		Cr	123.9[b]	SmA	124.4[b]	I
Pd	8	Cr	118.1 (12.6)			I
		Cr	89.5 (11.2)			I
	12	Cr	116.6 (19.9)	SmA	127.8 (0.88)	I
		Cr	63.1 (21.0)	SmA	124.4 (1.16)	I
	14	Cr	115.0 (21.8)	SmA	132.3 (0.92)	I
		Cr	72.2 (23.7)	SmA	128.0 (1.43)	I
	16	Cr	104.0 (14.3)	SmA	129.5 (1.18)	I
		Cr	53.9 (14.8)	SmA	127.6 (1.16)	I
	18	Cr	114.0 (21.4)	SmA	127.6 (1.16)	I
		Cr	83.7 (24.7)	SmA	123.8 (0.95)	I
VO	12	Cr	219.1 (9.01)	I		
		Cr	198.6 (8.58)	I		
	16	Cr	214.3 (9.63)	I		
		Cr	204.3 (9.58)	I		
FeCl	8	Cr	228.1 (7.54)	I		
		Cr	192.1 (7.83)	I		
	18	Cr	216.3 (10.1)	I		
		Cr	202.6 (10.6)	I		
5 Cu	14	Cr	193.3 (8.32)	I		
		Cr	183.7 (8.90)	I		
	18	Cr	188.1 (8.43)	I		
		Cr	183.3 (8.97)	I		

[a] The phase transition temperature (°C) and the enthalpies of transition (kcal mol^{-1}, in parenthesis) are given between the phases. *n* represents the number of carbon atoms in the alkoxyl chains; Cr is the crystal phase; SmA is the smectic A phase; and I stands for isotropic

[b] Unresolved peaks

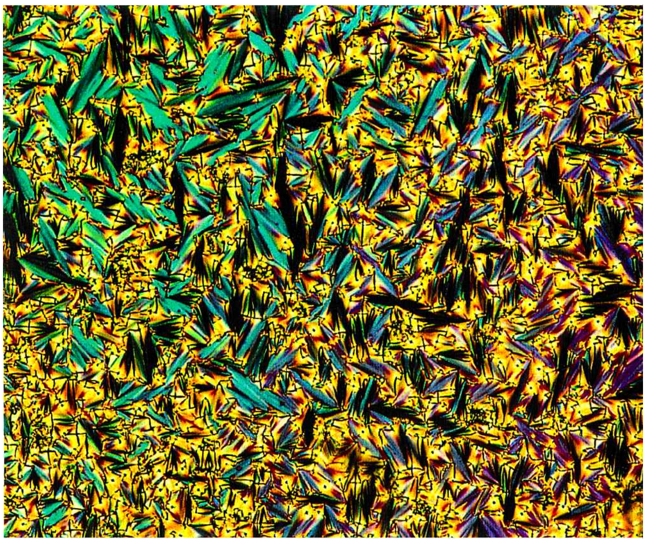
liquid crystallinity in these oxygen-bridged complexes was determined and controlled mainly by the geometric structure of the central metal cores incorporated.

4. Experimental

All chemicals for synthesis were reagent grades from Aldrich Chemical Co., and used without further purification. THF was dried over sodium benzophenone ketyl. Other solvents were purified and dried by standard techniques. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRS-200. Multiplicities are indicated as s (singlet), d (doublet), t (triplet) and m (multiplet). Infrared spectra were recorded on a Bio-Rad FTS-155 instrument using polystyrene as standard, and performed using Nujol mull methods between two KBr plates. DSC thermographs were obtained on a Perkin-Elmer DSC-7 calibrated with a pure indium sample at 156°C. All phase behaviours were determined at a scan rate of 10.0° min^{-1} unless otherwise noted. Optical polarized microscopy was carried out on a Nikkon MICROPHOT-FXA with a Mettler FP90/FP82HT hot stage system. Elemental analysis for carbon, hydrogen, and nitrogen was conducted on a Heraeus CHN-O-Rapid elemental analyser, and the results are reported in table 5.

4.1. *4-Dodecanoxy-2-hydroxybenzaldehyde*

This and the following sections give general procedure for the synthesis of 4-alkoxy-2-hydroxybenzaldehyde derivatives. The following procedures for monoalkylation are modified from literature methods to improve


(a)

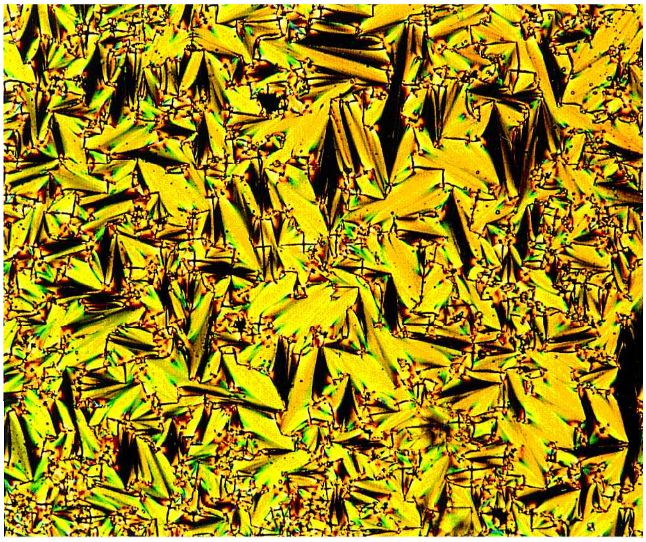

(b)

Figure 1. (*a*) Fan-texture observed by copper complex **4** ($n=10$, ×100) at 135°C; (*b*) fan-texture observed by palladium complex **4** ($n=14$, ×100) at 106°C.

the reaction yields. 2,4-Dihydroxybenzaldehyde (10 g, 0.07 mol), $KHCO_3$ (7.20 g, 0.07 mol), KI (catalytic amount) and 1-bromododecane (16.2 g, 0.07 mol) were mixed in 250 ml of dried acetone under a nitrogen atmosphere. The mixture was heated under reflux for 24 h, then filtered while hot to remove insoluble solids. Dilute HCl was added to neutralize the warm solution, which was then extracted twice with $CHCl_3$ (100 ml). The combined $CHCl_3$ extracts were concentrated to give a purple solid. The solid was purified by column chromatography eluting with a mixture of chloroform and hexane (V/V, 1/1). Evaporation of the solvents gave the product as a white solid. Yields 87–93%, m.p. 39.0°C. ^{1}H NMR (ppm, $CDCl_3$): 0.86 (t, $-CH_3$, 3H), 1.06–1.80 (m, $-CH_2$, 20H), 3.98 (t, $-OCH_2$, 2H), 6.38 (s, $-C_6H_3$, 1H), 6.52 (d, $-C_6H_3$, 1H), 7.39 (d, $-C_6H_3$, 1H), 9.68 (s, –CHO, 1H), 11.40 (s, $-C_6H_3OH$, 1H). ^{13}C NMR (ppm, $CDCl_3$): 14.17, 22.65, 25.87, 28.91, 29.23, 29.46, 29.55, 29.72, 31.91, 68.60, 100.9, 108.8, 114.9, 135.0, 164.4, 166.4, 194.2.

4.2. *4-Octadecanoxy-2-hydroxyacetophenone*

Literature procedures [6] were followed to prepare this compound. White needle crystals, yield 75–89%. ^{1}H NMR (ppm, $CDCl_3$): 0.84 (t, $-CH_3$, 3H), 1.23–1.80 (m, $-CH_2$, 32H), 2.48 (s, $-COCH_3$, 3H), 3.93 (t, $-OCH_2$, 2H), 6.33 (s, $-C_6H_3$, 1H), 6.40 (d, $-C_6H_3$, 1H), 7.53 (d, $-C_6H_3$, 1H), 12.69 (s, –OH, 1H). ^{13}C NMR (ppm, $CDCl_3$): 13.90, 22.49, 25.79, 28.82, 28.86, 29.13, 29.14, 29.17, 29.20, 29.40, 31.72, 31.74, 68.18, 101.1, 107.6, 113.5, 132.0, 165.1, 165.5, 202.1.

4.3. *4-Dodecanoxybenzylalcohol*

Under a nitrogen atmosphere, methyl 4-dodecanoxybenzoate (10.0 g, 0.015 mol) dissolved in 100 ml of dried THF was added dropwise to a THF solution of $LiAlH_4$ (1.32 g, 0.033 mol) at ice-bath temperature. The mixture was stirred at room temperature for 1 h, and then heated gently under reflux for 30 min. Dilute HCl (0.5M, 100 ml) was added to quench and neutralize the solution, which was then extracted twice with $CHCl_3$ (100 ml). The combined $CHCl_3$ extracts were concentrated to give a solid product. Recrystallization from acetone/methanol gave a white solid, yield 92%. ^{1}H NMR (ppm, $CDCl_3$): 0.86 (t, $-CH_3$, 3H), 1.24–2.16 (m, $-CH_2$, 20H), 3.94 (t, $-OCH_2$, 2H), 4.59 (s, $-CH_2OH$, 2H), 6.82 (d, $-C_6H_2$, 2H), 7.26 (d, $-C_6H_2$, 2H). ^{13}C NMR (ppm, $CDCl_3$): 14.10, 22.68, 26.13, 29.30, 29.49, 29.67, 29.78, 31.99, 32.01, 65.10, 68.17, 114.6, 128.7, 132.9, 158.9.

4.4. *4-Dodecanoxybenzylchloride*

Under a nitrogen atmosphere, to 4-dodecanoxybenzyl alcohol (10.0 g, 0.07 mol) dissolved in 250 ml of dried THF was slowly added $SOCl_2$ (5.50 ml, 0.075 mol) by means of an air-tight syringe at ice-bath temperature. The mixture was stirred at room temperature for 10 min, then ice water (10 ml) was added to destroy the excess of $SOCl_2$. The solution was extracted twice with $CHCl_3$ (150 ml), and the extract dried and concentrated to give a white solid. Recrystallization from acetone/methanol gave a white solid product, yield 82%. ^{1}H NMR (ppm, $CDCl_3$): 0.87 (t, $-CH_3$, 3H), 1.35–1.80 (m, $-CH_2$, 20H), 3.95 (t, $-OCH_2$, 2H), 4.48 (s, $-CH_2Cl$, 2H), 6.81 (d, $-C_6H_2$, 2H), 7.26 (d, $-C_6H_2$, 2H). ^{13}C NMR (ppm, $CDCl_3$): 14.14, 22.70, 25.60, 26.08, 29.26, 29.30, 29.41, 29.43, 29.77, 31.87, 46.36, 67.96, 114.6, 129.3, 130.0, 159.3.

Table 2. Phase behaviour[a] of metal complexes **6**.

Metal	n	Heating (top) Cooling (bottom)				
6 $M=\mathrm{Cu}$	8	Cr	213.5 (12.9)			I
		Cr	188.9 (9.56)	SmA	199.1 (1.66)	I
	10	Cr	206.8 (8.32)			I
		Cr	187.9 (6.04)	SmA	203.2 (2.25)	I
	12	Cr	187.2 (5.08)	SmA	193.3 (0.52)	I
		Cr	161.1 (3.30)	SmA	187.1 (1.39)	I
	14	Cr	197.9 (3.67)	SmA	201.7 (1.53)	I
		Cr	177.9 (8.89)	SmA	199.8 (2.29)	I
	16	Cr	198.2 (5.72)			I
		Cr	178.0 (5.46)	SmA	193.6 (1.68)	I
	18	Cr	196.2 (6.63)			I
		Cr	174.5 (5.41)	SmA	191.2 (2.04)	I
Pd	10	Cr	177.4 (7.26)	I		
		Cr	158.9 (7.87)	I		
	12	Cr	162.7 (6.51)			I
		Cr	120.1 (7.04)	SmA	159.4 (1.66)	I
	14	Cr	167.1 (11.3)	SmA	176.0 (1.13)	I
		Cr	141.9 (12.1)	SmA	171.0 (0.99)	I
	16	Cr	166.9 (12.5)	SmA	179.4 (2.13)	I
		Cr	144.0 (13.9)	SmA	175.8 (1.59)	I

[a] The phase transition temperature (°C) and the enthalpies of transition (kcal mol^{-1}, in parenthesis) are given between the phases. n represents the number of carbon atoms in the alkoxyl chains; Cr is the crystal phase; SmA is the smectic A phase; and I stands for isotropic

[b] Unresolved peaks

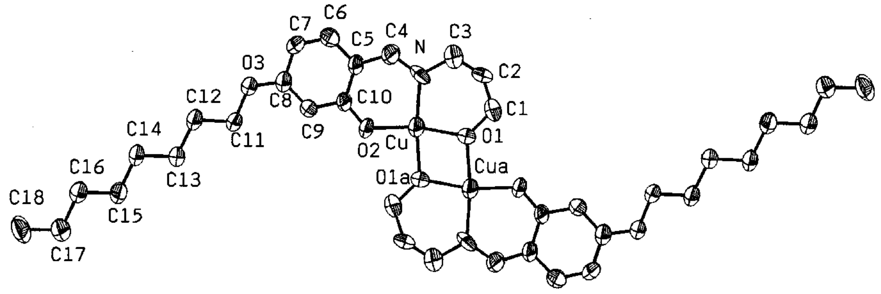


Figure 2. ORTEP drawing for copper complex (**4**; $n=8$) with the atomic numbering scheme.

4.5. *4-(4-Dodecanoxybenzoyl)-2-hydroxybenzaldehyde*

White crystals, yield 88%. ^{1}H NMR (ppm, $CDCl_3$): 0.86 (t, $-CH_3$, 3H), 1.07–1.82 (m, $-CH_2$, 20H), 3.99 (t, $-OCH_2$, 2H), 5.00 (s, $-CH_2O$, 2H), 6.48 (s, $-C_6H_3$, 1H), 6.59 (d, $-C_6H_3$, 1H), 6.90 (d, $-C_6H_4$, 2H), 7.24 (d, $-C_6H_4$, 2H), 7.48 (d, $-C_6H_3$, 1H), 9.69 (s, $-CHO$, 1H), 11.46 (s, $-C_6H_3OH$, 1H). ^{13}C NMR (ppm, $CDCl_3$): 14.78, 23.37, 26.70, 29.91, 29.95, 30.01, 30.21, 30.56, 32.56, 68.76, 70.79, 102.2, 109.6, 115.3, 115.9, 128.0, 130.0, 135.9, 160.0, 165.1, 166.7, 195.0.

4.6. *N-(3-Hydroxypropyl)-4-dodecanoxysalicylaldimine*

This and the following sections give general procedure for the synthesis of Schiff's base derivatives. 3-Amino-1-propanol (0.46 ml, 0.006 mol) in 10 ml of $CHCl_3$ was added by a syringe to a dried THF solution of 4-dodecanoxybenzaldehyde (20.0 g, 0.006 mol) in 100 ml of $CHCl_3$. The reaction mixture was heated under reflux for 3 h. Removal of $CHCl_3$ in vacuum gave a yellow solids; pale yellow microneedle crystals were obtained by recrystallization from THF/CH_3OH. Yield 94%, m.p. 72.0°C. ^{1}H NMR (ppm, $CDCl_3$): 0.86 (t, $-CH_3$, 3H), 1.27–1.78 (m, $-CH_2$, 20H), 1.94 (m, $-CH_2$, 2H), 3.60 (t, $-CH_2N{=}C$, 2H), 3.71 (t, $-CH_2OH$, 2H), 3.95 (t, $-OCH_2$, 2H), 6.30 (d, $-C_6H_3$, 1H), 6.33 (s, $-C_6H_3$, 1H), 7.06 (d, $-C_6H_3$, 1H), 8.10 (s, $-N{=}CH$, 1H). ^{13}C NMR (ppm, $CDCl_3$): 14.11, 22.64, 25.96, 29.03, 29.31, 29.52, 29.61, 29.65, 31.54, 31.88, 33.27, 53.14, 59.69, 68.03, 101.9, 106.8, 111.6, 132.7, 163.8, 168.1. IR (thin film): 2923, 2853, 1651, 1614, 1524, 1495, 1472, 1397, 1366, 1328, 1295, 1242, 1191, 1172, 1143, 1129, 1085, 1068, 1023, 1006, 914, 883, 846, 776, 744, 720, 638, 578 cm^{-1}.

Table 3. Crystallographic data and structure refinement for bis[*N*-(3-hydroxypropyl)-4-octanoylsalicylaldiminato] copper(II).

Chemical formula	$C_{36}H_{54}N_2O_6Cu_2$
Formula weight	737.92
Diffractometer used	Nonius
Space group	Monoclinic $P2_1/c$
a/Å	5.4908 (23)
b/Å	19.847 (5)
c/Å	16.636 (4)
β/°	96.87 (3)
Volume of cell/Å^3	1799.9 (10)
Z	2
Density/g cm^{-3}	1.362
Wavelength/Å	1.5418
$F(000)$	774
Unit cell: no.; (2θ range/°)	25; (21.82–45.76)
Scan type	$\theta/2\theta$
Scan width/°	$2\ (1.00 + 0.15 \tan \theta)$
Scan speed/° min^{-1}	2.06–4.12
$2\theta_{\max}$/°	120.0
$h_{\min}, h_{\max}$	-6, 6
$k_{\min}, k_{\max}$	0, 22
$l_{\min}, l_{\max}$	0, 18
Absorption μ/cm^{-1}	17.815
Crystal size/mm^3	$0.05 \times 0.08 \times 0.60$
Transmission	0.608; 1.000
Temperature/K	298
Measured reflections	2638
Observed reflections, $I > 2.0\sigma(1)$	1473
Unique reflections	2638
R_f^{a}; R_w^{b}	0.079; 0.074
G_0F^{c}	2.75
Refinement program	NRCVAX
No. of atoms	50
No. of refined parameters	208 (1473 out of 2638 reflections)
Minimize function	$\mathrm{sum}(w/F_0 - F_c/^2)$
Weight w	$1/\sigma(F_0)^2$
Weight modifier K in KF_0^2	0.000100
$(\delta/\sigma)_{\max}$	0.0097
Residual in final D-map (e/Å^3)	-0.620; 0.680

[a] $R_f = \mathrm{Sum}(F_0 - F_c)/\mathrm{sum}(F_0)$

[b] $R_w = \{\mathrm{Sum}[w(F_0 - F_c)^2/\mathrm{sum}(wF_0^2)]\}^{1/2}$

[c] $G_0F = \{\mathrm{Sum}[w(F_0 - F_c)^2]/(\text{no. of reflections–no. of parameters})\}^{1/2}$; 3 standard reflections (2, 0, 0; 0, 10, 0; 0. 0, 8) monitored every 3600 s, intensity variation <3%.

4.7. *N-(3-Hydroxypropyl)-4-(4-dodecanoxybenzoyl)-salicylaldimine*

Yield 90%. ^{1}H NMR (ppm, $CDCl_3$): 0.86 (t, $-CH_3$, 3H), 1.27–1.88 (m, $-CH_2$, 20H), 1.94 (m, $-CH_2$, 2H), 3.65 (t, $-CH_2N{=}C$, 2H), 3.74 (t, $-CH_2OH$, 2H), 3.95 (t, $-OCH_2$, 2H), 4.95 (s, $-CH_2O$, 2H), 6.43 (d, $-C_6H_3$, 2H), 6.86 (d, $-C_6H_4$, 2H), 7.02 (d, $-C_6H_3$, 1H), 7.29 (d, $-C_6H_4$, 2H), 8.10 (s, $-N{=}CH$, 1H). ^{13}C NMR (ppm, $CDCl_3$): 14.78, 23.37, 26.70, 29.91, 29.95, 30.01, 30.21, 30.56, 32.56, 53.38, 59.79, 68.04, 69.77, 102.4, 107.0, 111.9, 114.5, 128.1, 129.2, 132.7, 159.1, 163.0, 163.8, 168.1.

Table 4. Selected bonds/Å and angles/° for bis[*N*-(3-hydroxypropyl)-4-octanoylsalicylaldiminato]copper(II) complex. Symmetry code: $a = (1 - x, -y, -z)$.

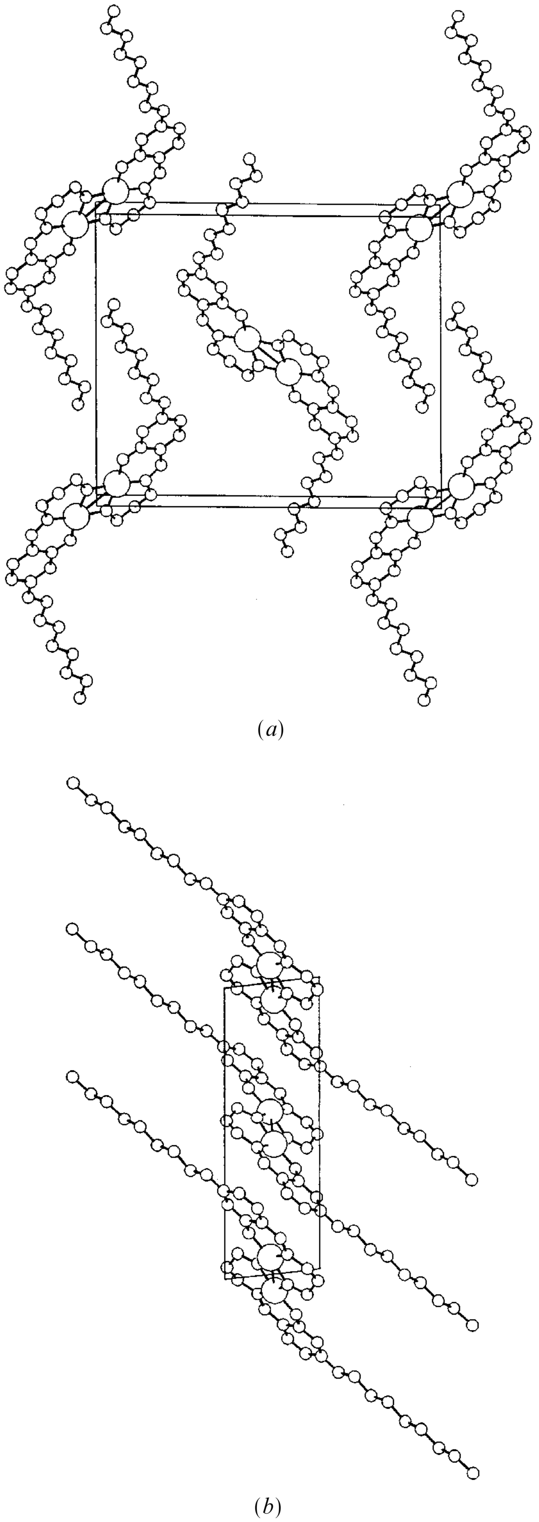
Cu–Cua	3.022 (3)	C4–C5	1.376 (14)
Cu–O1	1.914 (6)	C5–C6	1.398 (14)
Cu–O1a	1.921 (6)	C5–C10	1.444 (14)
Cu–O2	1.884 (6)	C6–C7	1.336 (15)
Cu–N	1.938 (8)	C7–C8	1.409 (15)
O1–Cua	1.921 (6)	C8–C9	1.387 (14)
O1–C1	1.394 (12)	C9–C10	1.375 (13)
O2–C10	1.287 (11)	C11–C12	1.485 (13)
O3–C8	1.328 (11)	C12–C13	1.504 (14)
O3–C11	1.437 (12)	C13–C14	1.503 (13)
N–C3	1.424 (13)	C14–C15	1.540 (14)
N–C4	1.331 (13)	C15–C16	1.501 (13)
C1–C2	1.439 (19)	C16–C17	1.528 (15)
C2–C3a	1.327 (19)	C17–C18	1.498 (15)
C3–C2a	1.327 (19)		
Cua–Cu–O1	38.08 (19)	N–C4–C5	129.6 (9)
Cua–Cu–O1a	37.93 (18)	C4–C5–C6	118.9 (9)
Cua–Cu–O2	130.63 (20)	C4–C5–C10	124.2 (9)
Cua–Cu–N	133.91 (24)	C6–C5–C10	116.9 (8)
O1–Cu–O1a	76.0 (3)	C5–C6–C7	123.4 (10)
O1–Cu–O2	92.7 (30	C6–C7–C8	120.4 (9)
O1–Cu–N	171.8 (3)	O3–C8–C7	116.5 (9)
O1a–Cu–O2	167.8 (3)	O3–C8–C9	125.5 (9)
O1a–Cu–N	96.0 (3)	C7–C8–C9	117.9 (9)
O2–Cu–N	95.4 (3)	C8–C9–C10	122.7 (9)
Cu–O1–Cua	104.0 (3)	O2–C10–C5	120.8 (8)
Cu–O1–C1	129.3 (6)	O2–C10–C9	120.5 (8)
Cua–O1–C1	126.1 (6)	C5–C10–C9	118.6 (8)
Cu–O2–C10	129.7 (6)	O3–C11–C12	109.9 (8)
C8–O3–C11	120.8 (7)	C11–C12–C13	112.9 (8)
Cu–N–C3	121.8 (7)	C12–C13–C14	113.7 (8)
Cu–N–C4	120.1 (6)	C13–C14–C15	113.1 (8)
C3–N–C4	118.1 (9)	C14–C15–C16	114.4 (8)
O1–C1–C2	115.9 (9)	C15–C16–C17	113.8 (8)
C1–C2–C3a	127.6 (17)	C16–C17–C18	113.3 (9)
N–C3–C2a	120.5 (11)		

4.8. *N-(3-Hydroxypropyl)-4-octadecanoxyacetophenomine*

Yellow solid, yield 85%, m.p. 92.0°C. ^{1}H NMR (ppm, $CDCl_3$): 0.82 (t, $-CH_3$, 3H), 1.23–1.85 (m, $-CH_2$, 32H), 1.95 (m, $-CH_2$, 2H) 2.25 (s, $-COCH_3$, 3H), 3.61 (t, $-CH_2{=}N$, 2H), 3.77 (t, $-CH_2OH$, 2H), 3.94 (t, $-OCH_2$, 2H), 6.14 (s, $-C_6H_3$, 1H), 6.22 (d, $-C_6H_3$, 1H), 7.27 (d, $-C_6H_3$, 1H), 16.79 (s, $-OH$, 1H). ^{13}C NMR (ppm, $CDCl_3$): 13.80, 14.02, 22.60, 25.94, 29.01, 29.27, 29.32, 29.49, 29.53, 29.61, 31.84, 32.06, 58.74, 67.82, 103.2, 105.7, 110.5, 129.6, 164.5, 171.7, 174.1.

4.9. *Bis[N-(3-hydroxypropyl)-4-dodecanoxysalicylaldiminato]copper(II)*

Copper acetate (0.15 g, 0.0008 mol) dissolved in 10 ml of hot CH_3OH was added to a chloroform (10 ml) solution of *N*-(3-hydroxypropyl)-4-dodecanoxysalicylaldimine (0.30 g, 0.0008 mol). The mixture was heated



(a)

(b)

Figure 3. Two different crystal packings of copper complex (**4**; $n=8$) viewed approximately down (*a*) the *a*-axis; (*b*) the *b*-axis.

Table 5. Elemental analysis of the metal complexes.

Metal	*n*	%C calcd (found)	%H calcd (found)	%Cl calcd (found)
4 Cu	8	58.59 (58.48)	7.38 (7.45)	
	10	60.50 (60.29)	7.87 (7.96)	
	12	62.16 (61.90)	8.28 (8.30)	
	14	63.62 (63.21)	8.67 (8.76)	
	16	64.90 (64.40)	9.00 (8.86)	
	18	66.04 (65.92)	9.30 (9.21)	
VO	12	61.67 (61.36)	8.23 (8.23)	
	14	63.14 (63.17)	8.61 (8.65)	
	16	64.45 (64.40)	8.94 (9.02)	
	18	65.60 (65.35)	9.24 (9.21)	
Pd	12	56.47 (56.430	7.54 (7.59)	
	14	58.12 (58.10)	7.93 (8.10)	
	16	59.59 (59.67)	8.27 (8.29)	
	18	60.91 (61.10)	8.58 (8.56)	
FeCl	8	54.49 (54.48)	6.86 (6.87)	8.94 (8.82)
	18	63.63 (63.86)	8.82 (8.86)	6.60 (6.51)
5 Cu	18	66.57 (66.41)	9.44 (9.40)	
VO	18	66.14 (66.21)	9.38 (9.40)	
6 Cu	8	63.20 (63.36)	2.95 (2.95)	
	10	64.45 (64.32)	2.78 (2.80)	
	12	65.57 (64.98)	2.64 (2.64)	
	14	66.58 (66.45)	2.50 (2.54)	
	16	67.49 (67.42)	2.38 (2.40)	
	18	68.32 (68.28)	2.28 (2.29)	
Pd	10	65.81 (65.95)	7.57 (7.62)	
	12	66.87 (66.73)	7.93 (7.84)	
	14	67.83 (68.02)	8.26 (8.33)	
	16	68.70 (68.92)	8.56 (8.57)	

gently under reflux for 5 h. The green-brown solution was concentrated under reduced pressure to give a brown solid; light brown crystals were obtained by recrystallization from ethyl acetate/methanol, yield 85%. IR (thin film): 2919, 2850, 1622, 1620, 1559, 1526, 1472, 1432, 1399, 1370, 1312, 1272, 1219, 1173, 1132, 1096, 1019, 990, 945, 843, 830, 789, 720, 660, 627, 601 cm^{-1}.

4.10. *Bis[N-(3-hydroxypropyl)-4-dodecanoxysalicylaldiminato]vanadyl (IV)*

Oxovanadium acetate (0.21 g, 0.0008 mol) suspended in 10 ml of hot CH_3OH was added to a chloroform (10 ml) solution of *N*-(3-hydroxypropyl)-4-dodecanoxysalicylaldimine (0.30 g, 0.0008 mol). The mixture was heated under reflux for 12 h under N_2. The brown solution was concentrated under reduced pressure to give a brownish solid; light grey crystals were obtained by recrystallization from dichloromethane/methanol, yield 83%. IR (thin film): 2917, 2850, 1609, 1534, 1470, 1430, 1408, 1358, 1306, 1273, 1227, 1206, 1131, 1071, 1038, 988, 938, 870, 845, 803, 768, 724, 635, 600 cm^{-1}.

4.11. *Bis[N-(3-hydroxypropyl)-4-dodecanoxysalicylaldiminato]palladium (II)*

N-(3-hydroxypropyl)-4-dodecanoxysalicylaldimine (0.30 g, 0.0008 mol) was mixed with palladium acetate

(0.20 g, 0.0088 mol) in 10 ml of THF under a nitrogen atmosphere. The mixture was heated gently under reflux for 1 day. The solution was filtered through Celite 545 to remove black insoluble solids, then concentrated to give a brown solid. A yellow solid was obtained by recrystallization from THF/methanol, yield 72%. IR (thin film): 2918, 2848, 1624, 1608, 1533, 1467, 1436, 1398, 1371, 1316, 1260, 1224, 1200, 1132, 1062, 1006, 943, 918, 823, 785, 721, 652, 618 cm^{-1}.

4.12. *Bis[N-(3-hydroxypropyl)-4-octanoxysalicylaldiminato]iron(III) chloride*

N-(3-hydroxypropyl)-4-octanoxysalicylaldimine (0.30 g, 0.0008 mol) was mixed with anhydrous ferric chloride (0.13 g, 0.0008 mol) in a glove box. Absolute ethanol (75 ml) was added to this mixture, and the resulting solution heated under reflux for 12 h under nitrogen gas. The solution was concentrated to give a brown solid; a reddish solid product was obtained by recrystallization from ethyl acetate/methanol (1/1), yield 86%.

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